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# Magnetic Structure of the Spin-Liquid State in a Frustrated Pyrochlore

M. J. Harris,<sup>1,\*</sup> M. P. Zinkin,<sup>1</sup> Z. Tun,<sup>2</sup> B. M. Wanklyn,<sup>1</sup> and I. P. Swainson<sup>2</sup>

<sup>1</sup>*Oxford Physics, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom*

<sup>2</sup>*Neutron and Condensed Matter Science, AECL Research, Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0*  
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The antiferromagnetic pyrochlores exhibit a high degree of frustration, resulting in a continuously disordered ground state. Neutron powder diffraction experiments have detected magnetic scattering similar in form to a liquid structure factor. We present a single crystal neutron scattering study of the pyrochlore  $\text{CsNiCrF}_6$  and quantify the anisotropy of the scattering. Using these data, we show that there are strong correlations between nearest-neighbor spins, and no significant longer correlations. This provides clear evidence for the liquidlike nature of the pyrochlore magnetic structure.

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Frustrated magnetic systems exhibit many phenomena resulting from strongly competing interactions such as spin-glass behavior, noncollinear and incommensurate ordering, and unusual critical properties. Recent theoretical and experimental work has focused on frustration in two-dimensional systems such as the triangular-lattice antiferromagnets (including the kagomé lattice), and in three dimensions the pyrochlores. In the pyrochlore structure, the magnetic ions sit at the corners of a framework of corner-sharing tetrahedra (shown schematically in Fig. 1), so that no spin configuration exists that will satisfy all six antiferromagnetic interactions on a single tetrahedron. The frustration may be partially overcome by the adoption of an ordered noncollinear structure, such as occurs in the pyrochlore  $\text{FeF}_3$  below about 15 K [1], but in general the ground state is infinitely degenerate with no long-range order at any temperature [2]. Any ordering that does occur is due to the effect of thermal fluctuations that break the degeneracy, resulting in the paradoxical situation of "order by disorder" [3].

The disordered ground state of the spin- $\frac{1}{2}$  triangular Heisenberg antiferromagnet has been described by Anderson [4] as being liquidlike, in the sense that in his resonating-valence-bond model the magnetic lattice condenses into a fluid of mobile valence bonds. This concept may also be applied to the disordered ground state that condenses in a geometrically frustrated lattice of classical spins. It should be emphasized that the spin-liquid state is distinct from that of a paramagnet, where the disorder arises from fluctuations which compete with a somewhat weaker exchange energy.

Extending the analogy with a classical fluid, we might expect the coherent scattering cross section,  $S(\mathbf{Q})$ , from a spin liquid to be rather different from that of a paramagnet, and to contain maxima and minima like a liquid structure factor. This reveals the presence of clusters with a finite correlation length. Neutron powder diffraction experiments have confirmed this assumption for many pyrochlores [5–8], as well as other compounds such as the kagomé lattice system  $\text{SrCr}_{8-x}\text{Ga}_{4+x}\text{O}_{19}$  [9]. However, the validity of the spin-liquid model for frustrated systems can only be ascertained fully by careful

single crystal measurements, where any anisotropy in the magnetic scattering can be analyzed. A preliminary single crystal measurement has been reported [10] showing that there is some anisotropy, but only a very qualitative interpretation could be given.

This Letter describes a thorough measurement and comparative simulation of the magnetic  $S(\mathbf{Q})$  for a pyrochlore with the composition  $\text{CsNiCrF}_6$ , using a single crystal sample. This compound is a member of the cubic pyrochlore family with the general formula  $\text{CsXYF}_6$ , where the magnetic  $X^{2+}$  and  $Y^{3+}$  ions ( $X=\text{Fe}, \text{Ni}, \text{Mn}$ ;  $Y=\text{Fe}, \text{Cr}, \text{V}$ ) are randomly distributed at the corners of

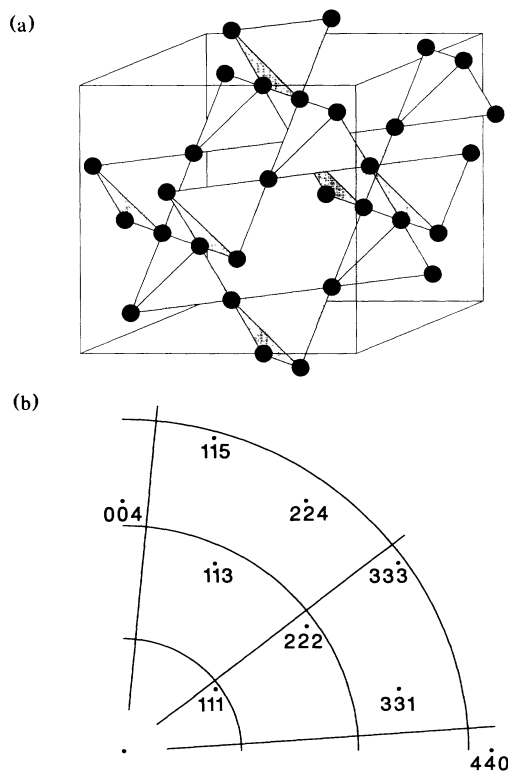


FIG. 1. (a) The pyrochlore crystal structure with only the tetrahedral framework of the magnetic atoms shown and (b) reciprocal space, with the scan trajectories marked.

the tetrahedral framework. Experimental studies suggest that while the exchange interactions given by the Curie-Weiss temperatures are relatively high in these materials—between 100 and 300 K—any magnetic ordering which may occur generally takes place below 10 K [11], and they must possess, therefore, a high degree of frustration.

In the rare earth pyrochlores such as  $\text{Tb}_2\text{Mo}_2\text{O}_7$  [7], there is no positional disorder, and the inherent frustration is purely geometrical in origin. However, in the fluoride pyrochlores the positional disorder of the magnetic ions further inhibits the development of ordered magnetic correlations. We expect, therefore, that the ground state of our  $\text{CsNiCrF}_6$  crystal is highly frustrated and represents a good example for spin-liquid behavior, which our experiments confirm.

Our measurements were performed using the C5 DUALSPEC and E3 triple-axis neutron spectrometers at the NRU reactor at Chalk River Laboratories. Both spectrometers were operated in the two-axis configuration, with a pyrolytic graphite (002) monochromator providing neutrons of wavelength 2.37 Å. The collimation both before and after the sample was set to be  $0.6^\circ$ , and a pyrolytic graphite filter was placed in the scattered beam to reduce spurious and thermal diffuse nuclear scattering, while leaving the essentially quasielastic magnetic scattering [7] unaffected. Two sets of sample measurement were made: one preliminary study at temperatures of 4, 30, 50, 70, and 90 K to obtain the approximate temperature dependence of the scattering, and the other, more detailed study at 12 and 150 K.

In each case, the crystal was mounted with the  $[1\bar{1}0]$  direction vertical, so that the scattering plane contained the reciprocal lattice vectors  $[440]$ ,  $[111]$ , and  $[004]$ . Two different types of scans were performed: radial scans very close to the  $[110]$ ,  $[111]$ , and  $[001]$  zones (but carefully avoiding the Bragg peaks), and then “ $\Psi$  scans” where the crystal was rotated about its vertical axis between the  $[110]$  and  $[001]$  zones, with the detector arm kept fixed in angle to give a constant magnitude of the wave vector transfer,  $Q$ . We show the trajectories of the scans in Fig. 1(b). Difference spectra were made by subtracting the high temperature from the low temperature scans. In this way, we were able to extract the coherent magnetic scattering, although this resulted in negative *relative* scattering [8]. Therefore, in order to facilitate comparison with our model we added a constant to the data, so that the coherent  $S(Q)$  is zero at  $Q = 0$ .

Diffuse scattering was observed to develop continuously below 30 K, and was strongest around the  $[110]$  zone. We show this development in Fig. 2, where a strong peak appears at about  $1.1 \text{ \AA}^{-1}$ , with a weaker peak at about  $2.3 \text{ \AA}^{-1}$ . This observation indicates dominant anti-ferromagnetic correlations, and is qualitatively similar to the results of previous experiments with powder samples of transition metal and rare earth pyrochlores [5–8] where peaks of diffuse scattering were observed at about  $1.1$

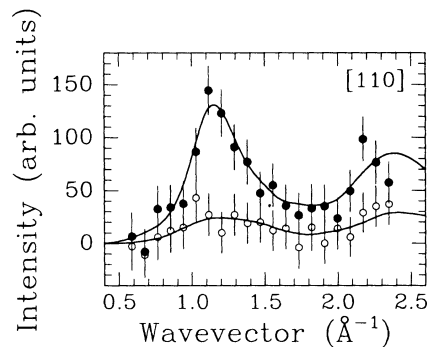


FIG. 2. Radial scans close to the  $[110]$  zone showing the coherent magnetic scattering at 4 K (full circles) and 30 K (open circles). The lines are guides to the eye.

$\text{\AA}^{-1}$  and  $2.2 \text{ \AA}^{-1}$ . The powder peaks represent a spherical average of the scattering, which may be expected to show some anisotropy in a single crystal experiment.

In Fig. 3 we show the difference spectra from the three radial scans close to symmetry zones for a sample temperature of 12 K. All three scans contain a strong peak of diffuse scattering at about  $1.1 \text{ \AA}^{-1}$ , together with weaker peaks at larger wave vectors. The scattering appears strongest along the  $[110]$  zone, but on the whole it is surprisingly uniform in the three scans for a given magnitude of the wave vector. The strong peak at  $1.1 \text{ \AA}^{-1}$  in particular appears to approximate a ring in reciprocal space, which is confirmed by the scans where only the crystal orientation angle,  $\Psi$ , was changed. The results of these scans are shown in Fig. 4. Here we display the

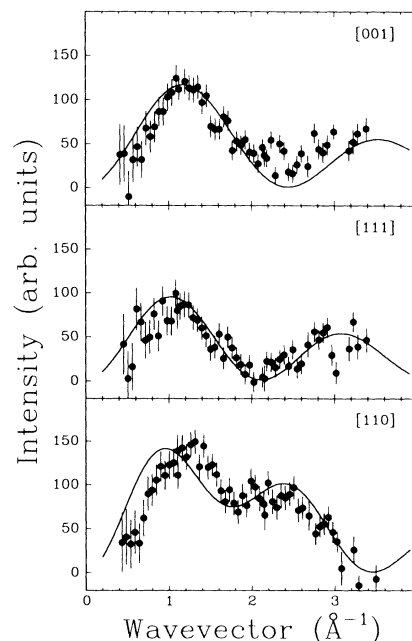


FIG. 3. Difference spectra for 12 K from radial scans measured close to the three symmetry zones  $[110]$ ,  $[111]$ , and  $[001]$ . The curves show a simulation of the expected scattering from a single tetrahedron.

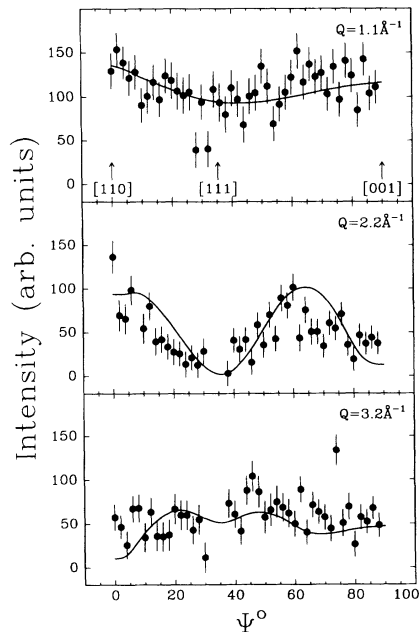


FIG. 4. Difference spectra from scans where the crystal angle,  $\Psi$ , was changed while the detector arm was kept fixed, thus resulting in a constant  $Q$  for each scan. The positions of the  $[110]$ ,  $[111]$ , and  $[001]$  zones in  $\Psi$  are shown, and the results of the simulation are shown as curves.

intensity variation for three different wave vector transfers across the whole of one quadrant of the scattering plane. The first  $\Psi$  scan, at the main peak of the scattering ( $Q = 1.1 \text{ \AA}^{-1}$ ), shows only a very slight variation in the intensity of the diffuse scattering across the quadrant. The second scan (with  $Q = 2.2 \text{ \AA}^{-1}$ ) shows a more pronounced  $\Psi$  dependence, with maxima corresponding roughly to the  $[110]$  and  $[113]$  zones, and a minimum at the  $[111]$  zone. The final scan (with  $Q = 3.2 \text{ \AA}^{-1}$ ) shows practically no variation in the intensity with  $\Psi$ . Hence, although the scattering exhibits some anisotropy, the strongest part (where  $Q = 1.1 \text{ \AA}^{-1}$ ) is relatively uniform. It has been noted previously [7] that the diffuse scattering seen in powder diffraction studies is reminiscent of a liquid structure factor. Our single crystal experiments confirm that this appears to be the case, which is a surprising result from a three-dimensional, crystalline solid.

By way of analyzing the diffuse scattering, we have performed calculations of the magnetic scattering cross section from a single tetrahedron of magnetic ions in the unit cell. Our simulation of  $S(\mathbf{Q})$  was achieved by varying the directions of the four spins on the model tetrahedron until we obtained a result that appears to be qualitatively similar to the experimental data. For each spin configuration, the cubic symmetry of the crystal was accounted for by generating all symmetry-related configurations and calculating an average  $S(\mathbf{Q})$  from them. This means that our calculation does not distinguish one symmetry-related  $\mathbf{Q}$  from another, as should be the case

for a magnetic system with no long-range order. The primary constraint for the selection of candidate configurations was that the net magnetization of each is zero.

In Figs. 3 and 4 the results of the simulation are shown by curves superimposed on the experimental data. A gently sloping background was included in the model to account for the oversubtraction of thermal diffuse scattering when extracting the difference spectra. It should be emphasized that only a single scale factor was used to scale all of the intensities of the calculated results with the experimental data. It is clear that the simulation gives a very good description of the data. In particular, it predicts the widths of the observed diffuse peaks very closely. This suggests that the coherent scattering at 12 K is almost entirely due to correlations within individual tetrahedra, with no longer-ranged correlations involved. Since a tetrahedron consists of only four magnetic atoms, each at a tetrahedral vertex, no shorter-ranged ordering scheme can exist. The intense frustration in the pyrochlore lattice thus prevents any ordering over a length scale longer than a single nearest-neighbor distance. Note that the diffuse peaks shown in Fig. 2 for a sample temperature of 4 K are slightly sharper than those predicted by the model, indicating the onset of slightly longer-ranged interactions at low temperatures that include some next-nearest neighbors. In fact, the ac susceptibility of  $\text{CsNiCrF}_6$  shows evidence of a gradual increase in order below about 40 K and a spin-glass anomaly at 8 K [12]. We surmise that the diffuse scattering data at 4 K must represent the correlations in the spin-glass phase, while those at 12 K represent the spin-liquid state.

The spin configuration which gives the best agreement with the observed scattering ( $\chi^2 \sim 1.5$ ) is detailed in Table I and shown schematically in Fig. 5. In this configuration there is a strong anisotropy lying along the  $\langle 100 \rangle$ -type directions. An additional, but smaller component is also present along the  $\langle 110 \rangle$ -type directions. This spin structure is largely antiferromagnetic, with some inevitable ferromagnetic correlations. It represents a time average of what is really a dynamic process, but reveals the character of the short-range order. For comparison, an alternative configuration such as the  $\text{FeF}_3$  type—which is discussed later—gives a less satisfactory description of the data ( $\chi^2 \sim 2.3$ ).

TABLE I. The spin configuration which gives the best agreement with the experimental data. The coordinates of the four atoms used in the unit cell are given as  $x$ ,  $y$ , and  $z$ , and the crystallographic direction along which each spin points as the components  $i$ ,  $j$ , and  $k$ .

	$x$	$y$	$z$	$i$	$j$	$k$
1	0	0	0	1	1	4
2	$\frac{1}{4}$	$\frac{1}{4}$	0	2	2	$\bar{4}$
3	$\frac{1}{4}$	0	$\frac{1}{4}$	$\bar{2}$	$\bar{2}$	$\bar{4}$
4	0	$\frac{1}{4}$	$\frac{1}{4}$	$\bar{1}$	$\bar{1}$	4

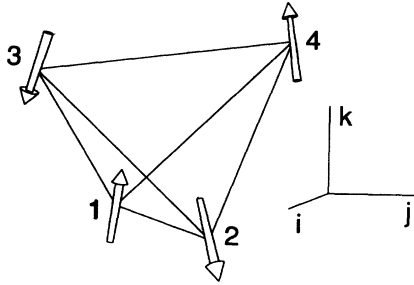


FIG. 5. Schematic view of a single tetrahedron showing the spin configuration which gives the best agreement with the experimental data.

This overall behavior may be understood as a result of the intriguing phenomenon of order by disorder [3]. Henley [13] has shown that the frustrated face-centered-cubic antiferromagnets prefer to order into collinear structures at finite temperatures. This is because the entropy favors the ground state with the greatest density of low-energy excitations, which in these cases is an ordered collinear structure. Hence, for finite temperatures we might expect that the pyrochlore lattice will choose a collinear structure. This may not necessarily be a long-range ordered structure, but simply a tendency for the essentially dynamic short-range order to average out to this type of configuration. It appears that this occurs in  $\text{CsNiCrF}_6$ , as the spins lie predominantly along the  $\langle 100 \rangle$ -type directions in our model.

The previous single crystal study of  $\text{CsMnFeF}_6$  and  $\text{CsNiFeF}_6$  [10] has revealed somewhat different results from ours for  $\text{CsNiCrF}_6$ . In the cases of  $\text{CsMnFeF}_6$  and  $\text{CsNiFeF}_6$ , the strongest scattering occurs along the  $[111]$  zone, and is weakest along  $[001]$ . Using our simulation program, we found that this scattering is more compatible with a short-range ordering of the  $\text{FeF}_3$  type [1], i.e., with spins adopting a noncollinear arrangement along the  $\langle 111 \rangle$ -type directions. The spins all point directly into (or away from) the center of each tetrahedron in this model. Furthermore, the scattering from these two compounds is substantially sharper in width than that from  $\text{CsNiCrF}_6$  for the same temperature, indicating that the correlations in them are rather longer ranged. The reason for these differences is not clear since we also expect uniaxial anisotropy along the  $\langle 111 \rangle$  directions in  $\text{CsNiCrF}_6$  [14]. However, it is safe to conclude that the resulting balance between entropy considerations, the frustrated exchange interactions, and crystalline anisotropy is sufficiently different in  $\text{CsNiCrF}_6$  from those in  $\text{CsMnFeF}_6$  and  $\text{CsNiFeF}_6$  to result in a different short-range ordered scheme. In our case it ap-

pears to choose the expected collinear structure from the continuously degenerate ground state, albeit on an extremely short length scale.

In summary, we have measured the diffuse magnetic neutron scattering from a single crystal of the frustrated pyrochlore  $\text{CsNiCrF}_6$ . The form of  $S(\mathbf{Q})$  is liquidlike in nature, reflecting the essentially dynamic structure and very short-range order present. The scattering may be described extremely well by a model that consists of only a single tetrahedron of magnetic atoms, with each spin possessing a dominant component along either the  $[001]$  or the  $[00\bar{1}]$  direction.  $\text{CsNiCrF}_6$  attempts, therefore, to select an ordered state out of its infinitely degenerate ground state, but can only do so on an extremely short length scale. In this sense, the magnetic structure is clearly very similar to the liquid state.

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\* Present address: ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, United Kingdom.

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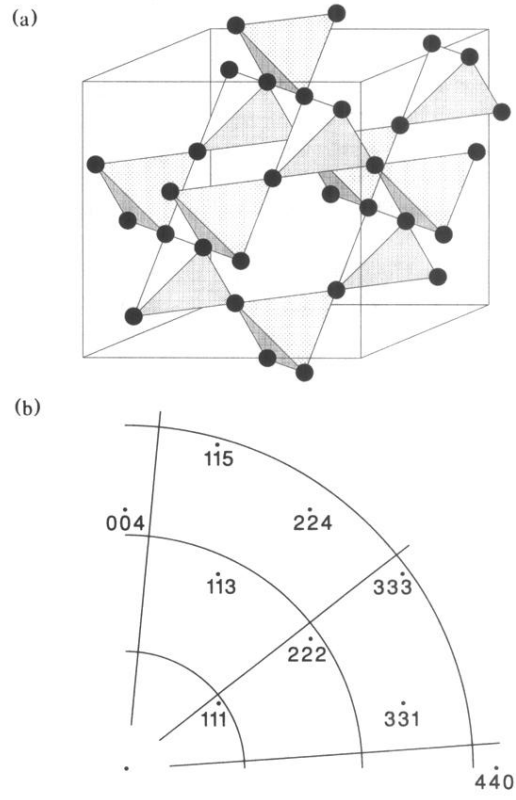


FIG. 1. (a) The pyrochlore crystal structure with only the tetrahedral framework of the magnetic atoms shown and (b) reciprocal space, with the scan trajectories marked.